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HARDENING TIMES FOR CASING CEMENTATION.*

By N. Healey, B.Sc., and S. L. Pease, B.S., B.A., F.G.S.

The ideal hardening time to be allowed for cement used in casing cementations is admittedly difficult to determine, and standing times actually applied are necessarily to some extent arbitrary. With increasing experience and accumulated empirical data, however, it has gradually been

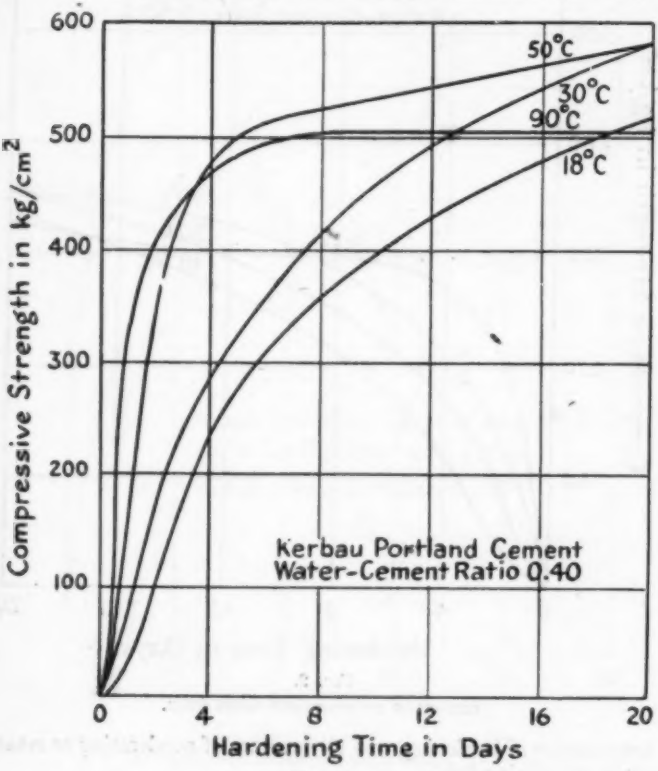


Fig. 1.

VARIATION OF STRENGTH WITH TIME

found possible to reduce standing times without any unfavourable effect on the efficacy of water shut-offs. At the same time, scientific testing of the cements used has led to the adoption of certain criteria as to the properties required as a basis for specifications, although the extent to which

* Paper received 8th October, 1941.

these criteria really represent what is required of the cements under sub-surface conditions is not completely known.

Before discussing the actual hardening times to be adopted, the influence of various factors affecting the rate at which cement acquires its strength will be considered.

The principal of these factors are: (1) water-cement ratio of the slurry,

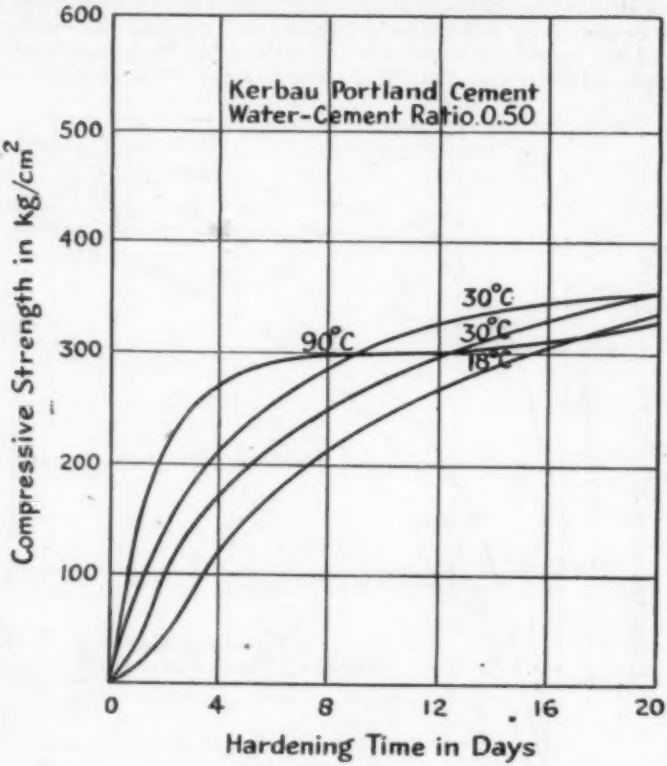


FIG. 2.

VARIATION OF STRENGTH WITH TIME.

(2) temperature of hardening, and (3) presence of accelerating or retarding agents in the mixing fluid.

The accompanying graphs show the influence which those factors have in the rate of increase of the compressive strength of the cement, which property has been found to be a satisfactory indication of the suitability of the cement for casing cementations.

Time Factor

The shape of all the strength–time curves (Figs. 1 and 2) shows that the rate of hardening is greatest initially, which is of course very advan-

taneous, indicating that a high proportion of the final strength is obtained in the first day.

Water–Cement Ratio

The lower the water–cement ratio of a slurry the more rapidly it hardens. This is illustrated by a comparison of Figs. 1 and 2. Fig. 5 shows the variation of the compressive strength of "Kerbau" Portland cement for different water–cement ratios at temperatures of 50° and 90° C.

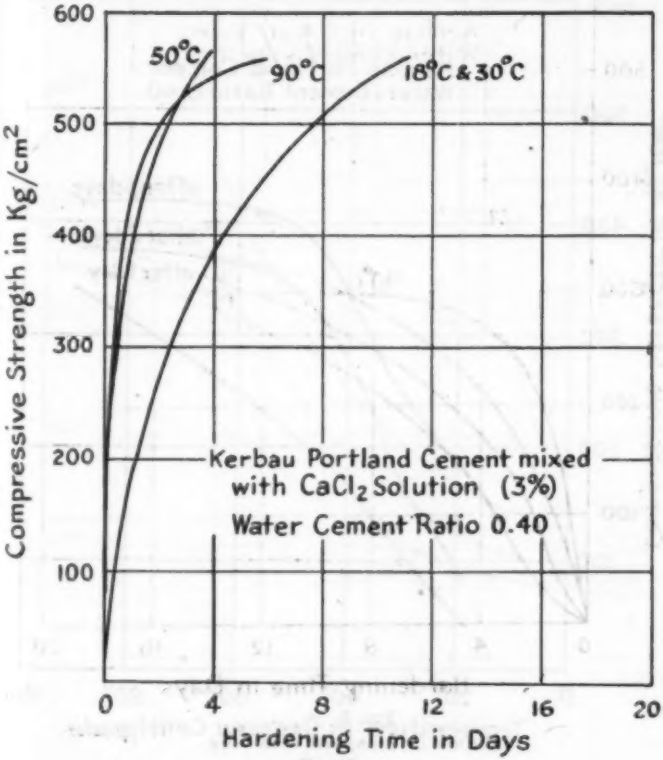


FIG. 3.

VARIATION OF STRENGTH WITH TIME

An average cement slurry for oil-field purposes has a water–cement ratio of 0·40 (S.G. 1·92), and, as Fig. 1 shows, such a slurry hardens very rapidly at 50° C., the temperature normally obtaining at a depth of about 2300 feet, according to the geothermal gradient.

Temperature

As shown by Fig. 4 and the time–strength graphs, an increase in temperature results in an acceleration of the hardening process. This effect is

chiefly noticeable in the initial strength. (After long periods of hardening at high temperatures, the strength is often not as high as for the same period at lower temperatures—*e.g.*, 90° curves on Figs. 1 and 2.)

This temperature effect is important in oil-well cementations on account of the increase in temperature with depth. If the surface temperature is assumed to be 86° F. (30° C.), with a geothermal gradient of 1° F. per 64 ft., the temperature at 3000 feet will be 133° F. (56° C.). From Fig. 4

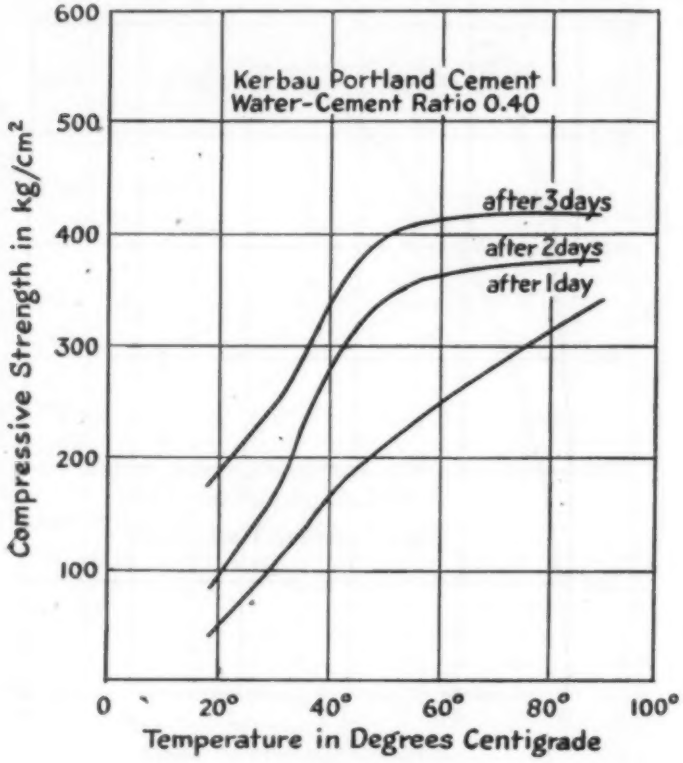


FIG. 4.

VARIATION OF STRENGTH WITH TEMPERATURE.

it can be seen that slurry with a 0·40 water–cement ratio has more than twice the compressive strength after one day at 50° C. than it has at 30° C. Therefore, at 3000 feet the cement will be more than twice as strong after one day as it would be at the surface.

The cement slurry, of course, does not immediately assume the geothermal temperature as it is pumped down the bore-hole, and this is a favourable condition for placing the cement, in that the time of initial set of the slurry is not unduly decreased by depth. This temperature lag

probably does not last long enough to affect the strength, however, since the heat generated by the cement in setting also tends to raise the temperature of the thickening slurry.

Replotting the information on Figs. 1, 2, and 3 with the temperatures converted to depths according to the geothermal gradient, Fig. 6 was obtained.

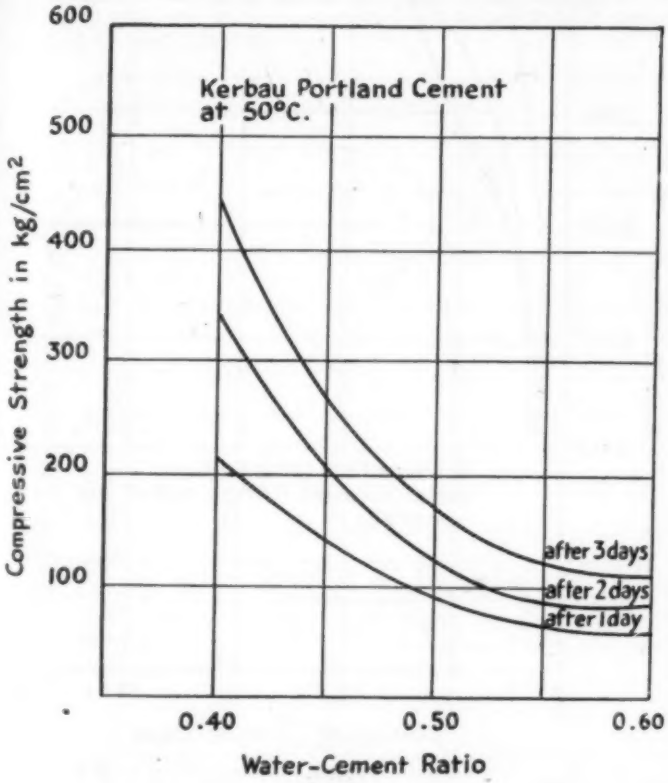


FIG. 5.

VARIATION OF STRENGTH WITH WATER–CEMENT RATIO.

These graphs show the time required for a slurry to attain a compressive strength of 50 kg./cm.².

Accelerators and Inhibitors

The effect of accelerators (*e.g.*, $CaCl_2$) is illustrated for a Portland cement by a comparison of Figs. 1 and 3. In every case the use of a 3 per cent. solution of calcium chloride as the mixing liquid results in an increase in the initial compressive strength. However, accelerators also have the unfavour-

able effect of decreasing the time of initial set, so they are not used if sufficient early strength is obtainable without them.

Inhibitors such as lead or zinc compounds, quebracho and boric acid retard the hardening of cements. They are not frequently used, however, because a slight excess may prevent the slurry from developing any strength at all.

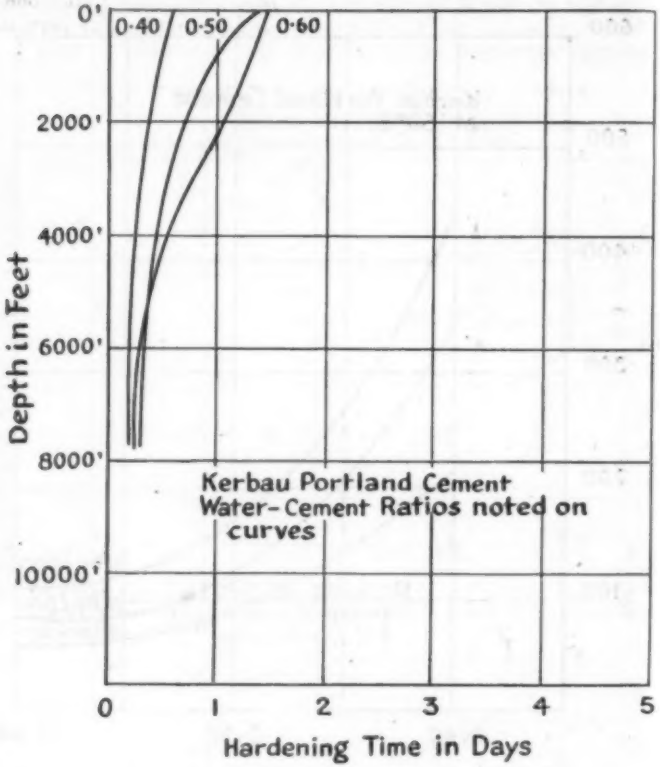


FIG. 6.

VARIATION WITH DEPTH OF TIME REQUIRED TO ATTAIN STRENGTH OF 50 KG./CM.^{2}.

Application of Principles to Oil-field Practice.

It is not known exactly what kind of strength requirements an oil-well cement has to meet, but it is reasonable to assume that resistance to shock is an important consideration, and that this is related to compressive and tensile strengths. A large number of tests indicate that compressive strength is probably a more reliable indication of this property than tensile strength.

Experience has shown that development of a certain compressive strength after a given time actually is a good criterion. The type of cement (Class III)

used by the Shell Group for cementations above 3000 ft. has to meet the following specifications :—

Water–Cement Ratio.	Temperature.	Compressive Strength. After 1 day.	Compressive Strength. After 3 days.
0·50	30° C.	50 kg./cm.^{2}	100 kg./cm.^{2}

This type of cement has proved to be sufficiently strong after one day's setting to resist any shock occurring in drilling and to give permanently satisfactory water shut-offs.

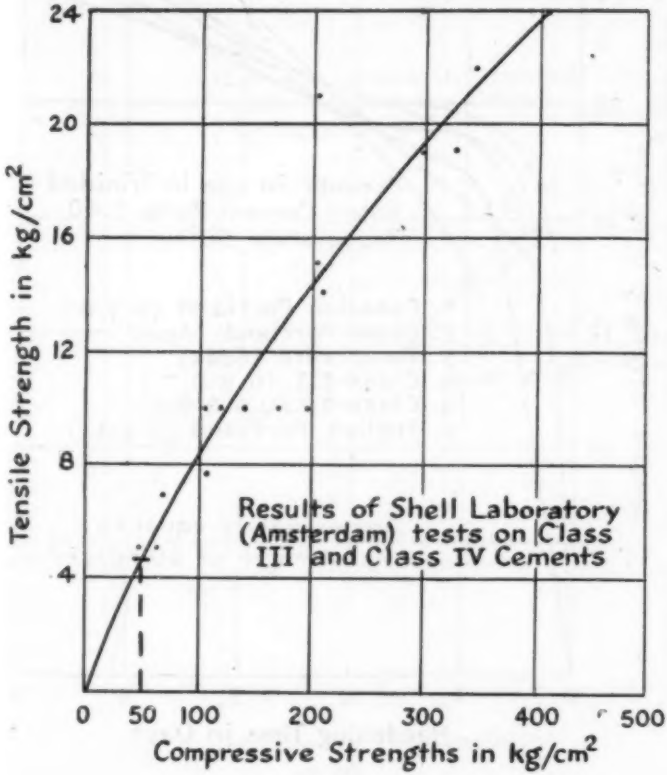


FIG. 7.

RELATION BETWEEN TENSILE AND COMPRESSIVE STRENGTHS.

The type of cement (Class IV) used below 3000 ft. has to meet the following specifications :—

Water–Cement Ratio.	Temperature.	Compressive Strength. After 1 day.	Compressive Strength. After 3 days.
0·60	50° C.	50 Kg./cm.^{2}	100 Kg./cm.^{2}

The strength requirements are the same but, allowing for a higher

temperature, the strength must be obtainable with a higher water–cement ratio.

The cement is actually used at depths corresponding to geothermal temperature higher than 50° C. and with a water–cement ratio of about 0·40. Fig. 5 shows that after one day at 50° C. a cement with a water–cement ratio of 0·40 has a compressive strength more than three times as great as one with a ratio of 0·60 under similar conditions. If the cement

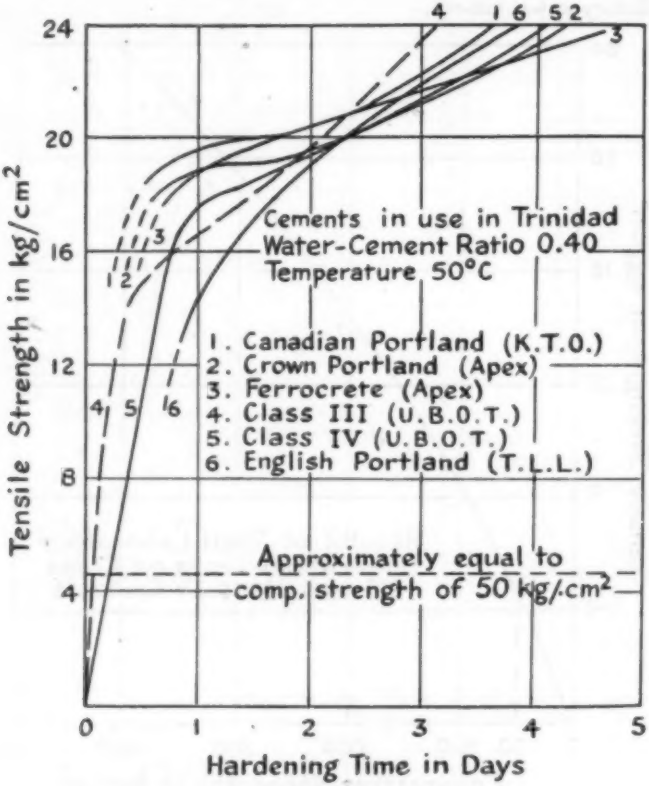


FIG. 8.

VARIATION OF STRENGTH WITH TIME.

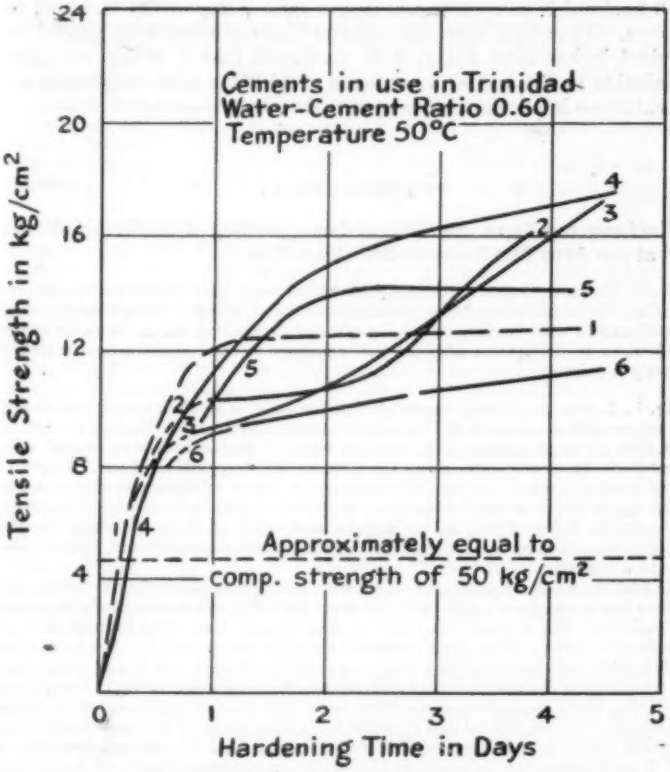
meets specifications, therefore, we may assume that as used in the field, it will have a compressive strength of ÷150 kg./cm.² after 1 day. This is about three times the strength which experience has shown to be necessary to allow drilling out after 1 day, and hence an allowable setting time of 1 day also below 3000 ft. appears to be safe and reasonable.

It follows from the foregoing that the desirable hardening time can be based on the attainment of a compressive strength of 50 kg./cm.², and

Fig. 6 shows that the time required to reach this strength at depths below 3000 ft. is considerably less than 1 day.

Quality of Cements in use in Trinidad

That oil-well cements in use in Trinidad at present are a good deal better than is required by the above specifications was proved by a series of tests made on samples collected from several companies. The results are shown on Fig. 8.



1. Class III (U.B.O.T.)
2. Canadian Portland (K.T.O.)
3. Crown Portland (Apex)
4. Class IV (U.B.O.T.)
5. Ferrocrete (Apex)
6. English Portland (T.L.L.)

FIG. 9.

VARIATION OF STRENGTH WITH TIME.

Tensile strengths were determined for these samples, as no apparatus was available for determining compressive strengths, but an approximate relationship existing between the two properties is indicated by Fig. 7. The tensile strength corresponding to a compressive strength of 50 kg./cm.^{2} is seen to be about 5 kg./cm.^{2}.

In view of the location of the curves in relation to this value and of the grouping of the other curves about those for Class III and Class IV cement (Fig. 9) whose compressive strength has already been shown to be about three times stronger than specifications, it is evident that the requirement of 50 kg./cm.^{2} is easily attained in less than 1 day at 50° C. by all these cements. Therefore, since the necessary strength has been proved to be acquired in less than 1 day, it is considered that it should certainly be permissible to drill out at a minimum of 24 hours after completing casing cementations in all cases where a normal cement is used.

DISCUSSION.

The foregoing Paper was discussed at a meeting of the Trinidad Branch held at the Apex Clubhouse on 28th May, 1941.

MR. N. HEALEY (United British Oilfields of Trinidad, Ltd.), before reading the paper, remarked that the title might be a little misleading, the object being to prove that the normal cement used by any of the Companies in Trinidad was sufficiently strong to enable it to be drilled out after 24 hours instead of the normal 3 days which were formerly required.

MR. L. A. BUSHE (Apex), congratulating the authors on their paper, said that they had apparently established the fact that cements used in Trinidad were sufficiently hard after 24 hours' setting time to allow work in the well to be continued without harmful effects on the water shut-off. Prior to the completion of the authors' tests, it had been necessary for Trinidad operators to allow minimum hardening times of 3 days below 3000 feet and 6 days above 3000 feet, in accordance with Drilling Regulations, and he believed that it was largely as a result of these tests that permission had now been given by the Government Petroleum Technologist to reduce the hardening time to a minimum of 24 hours.

He had one small criticism, not destructive in any way—namely, that although the authors had been at some pains to point out that 1 day was a sufficiently long hardening period for the cement, yet three of their graphs were only divided into 4-day periods and went up to 20 days, so that it was difficult to read the details accurately. With a fairly fine pencil he had tried to sub-divide Figs. 1 and 4, and found that he got considerable differences between the two. He found that in Fig. 1 after 1 day at 30° C. they had a strength of about 75 kg./cm.^{2}, whereas in Fig. 4 he made the strength 100 kg./cm.^{2} It seemed to him it would have been better if the scale had been considerably larger, so that they could discover exactly what the strength was, say, after 1, 2, 3, and 4 days, for, so long as the trend was an increase in hardness, he did not see that they were concerned what the result was after 3 or 4 days.

The authors had laid down a " yardstick " of 50 kg./cm.^{2}, and it would be interesting to hear what others present had to say about the strength necessary to make an effective water shut-off. He saw no reason to doubt the adequacy of the specification, and, accepting that, they found that with all the cements in use in Trinidad 1 day was ample below 3000 feet even with a water/cement ratio as high as 0·60.

Similarly with shallow depths it was only necessary to reduce the water/cement ratio to 0·40 to obtain the desired strength in 1 day.

As these results were obtained without an accelerator, he would like to ask the authors if they recommended the use of an accelerator at all. Did they know whether calcium chloride had a corrosive effect on steel casing? It was not allowable,

he believed, in many cases for use in reinforced concrete, as it was alleged that it corroded the steel reinforcing.

Had the authors any knowledge of what water–cement ratios actually were in use in Trinidad?

Finally, was the geothermal gradient of 1° in 64 feet correct for Trinidad? As a rough guide they had always talked of 1° in 100 feet, and it seemed to him that 1 in 64 was a little high.

MR. HEALEY wished to apologize about the graphs, as the work had been done outside, and those were the graphs furnished. It was rather difficult to make out, as the graphs were reproduced roughly, but were they quite so much out as Mr. Bushe said?

The geothermal gradient given was a general average, but he thought from experience in the United States it was actually on the low side for oil-fields, 1° F. in 50 feet being normal.

As to the effect of calcium chloride, he said that his company had stopped using it now, and he could not see any real reason for using it on these results.

As for corrosive action of calcium chloride, he could not say that any had been noticed in practice.

The specification of compressive strength of 50 kg./cm.^{2} had been arrived at from experience in the field, and all specifications were based on this at the moment.

MR. G. H. SCOTT (Apex) said he had intended to bring up the same point as to how the authors arrived at the empirical figure of 50 kg./cm.^{2} as the correct specification for cement. He felt that laboratory tests were so liable to be very much higher than the actual cement strengths underground. For instance, the cement was liable to contamination by mud, as well as to the possibility of aeration of the grout after placement; and also in test samples the excess water could settle out and rise to the surface, whereas underground it was liable to be trapped. He gave it as his considered opinion that water formed a vesicular structure in the cement which would affect both compressive and tensile strengths deleteriously. He wished to know in how far the safety factor of 3 could be decreased by the factors he had mentioned—that is to say, aeration of the grout, contamination of the mud, and excess water.

He had never seen before an actual curve that related compressive to tensile strength, and thought most cement manufacturers would definitely refuse to give any correlation between tensile and compressive strength. He enquired what others thought on how impact strength varied with compressive and tensile. Another thing was the shear strength, and it struck him, from his knowledge of what sheer forces could do underground, that 50 kg./cm.^{2} compressive was rather low if there was any weight on the casing string.

He wished to know further details of the cement specification, especially as to the limits of hydraulic modulus, and if they had any actual limits for viscosity with time in the placing of the cement.

MR. HEALEY, replying to the question as to the effect of mud and free water, etc., said he did not really see how that affected one's taking 50 kg./cm.^{2} as a criterion in so far as results were actually based on field-scale tests after laboratory tests. It was found that a cement with this compressive strength was sufficiently hard under field conditions. Admittedly things could go wrong under exceptional conditions such as Mr. Scott suggested, but normally if a cement were taken which came up to this specification, a good cement job was normally obtained in the field.

MR. SCOTT said that Reid and others recommended a tensile strength of 250 lb./sq. in. for cement grouts.

MR. HEALEY replied that his company no longer had tensile strength in their specifications.

MR. SCOTT remarked that, accepting Mr. Healey's 50 kg./cm.^{2} compressive as equivalent to 5 kg./cm.^{2} tensile, that was round about one-third of the tensile strength

recommended by other authorities. In shear about 75 kg./cm.² was usually recommended by people in the States.

Mr. Healey replied that the relationship drawn between tensile and compressive was purely empirical. As could be shown from the graph, a point corresponding to 5 kg./cm.² tensile strength and 50 kg./cm.² compressive strength had been taken, and a line drawn through this point and the origin. The mean of the points came pretty near to this.

As to the effect of mud on cements, laboratory tests had been made, and normal shale muds thoroughly mixed into cements up to 3 per cent. did not normally have any effect on hardening, but above 3 per cent. deleterious action was observed.

On the question of impact compared with tensile and compressive strengths, he did not think much was known about that. He thought it was more related to compressive than to tensile strength. The hydraulic modulus was the usual one for cement specifications, namely, 1·7–2·2 and the silicate modulus 1·2 to 4·0.

Mr. G. S. Taitt (U.B.O.T.) wished to emphasize that the paper was a rather good example of engineering practice because the authors had collected quite a lot of essential data and had related it to this very empirical figure of 50.

Mr. Scott had asked what the real value of that figure was. It was simply the result of experience in the Shell group, and it was found not by any calculated method that it would be a suitable strength, but that cements as used on the basis of past practice, purely from an empirical point of view, had a strength of about 50 kg./cm.², and so the whole question of the strengths of the cements actually used (up to 3 times the 50 kg. in many cases) were all related to empirical information.

He would like to bring out that they were really working rather in the dark as regards cement strengths, and they did not know whether tensile, or compressive, or what other strength, was the best criterion. It had been suggested that the main function of the cement was to act as a filler to prevent water infiltration, and that strength did not really matter, and it was not quite certain what properties actually were wanted. It had been suggested that cement of a very low strength but of a very good sealing power might be what was desirable.

Mr. Scott had brought out a point about the actual condition of the cement in the hole in comparison with the results in the laboratory. There was usually a good factor of safety, in comparison with the factor of 50, in the cements in use; but in any case he wished to mention that cement in open hole was very much harder to drill out as a rule than cement in casing. In the casing, water could not get out of a cement, with the result that the strength might be somewhat lower than in laboratory tests, whereas in open hole the water had a chance of escaping into porous formations and the strength of the cement was probably not much reduced below the laboratory criterion.

Mr. J. W. Knights (Apex) asked what mechanical means were used to obtain the water ratio to be sure of a steady grout.

Mr. Healey said he presumed Mr. Knights meant in the field; it was a matter of trial and error; the grout was weighed as it came through. But automatic feeders were now being developed in the United States and the water supply could be regulated so that the slurry came through at the required weight.

Mr. H. C. H. Darley (Trinidad Leaseholds Ltd.) asked if, when the authors spoke of a successful cement job, they meant that no subsequent trouble was experienced with water, or whether the job was able to stand some sort of test.

With regard to temperature gradient, he had found that mud temperatures varied as much as 10° F. or more for the same depth in different parts of the same field. He had known one well, where the bottom-hole temperature taken with a bottom-hole thermometer actually dropped some 20° F. on going deeper. He only mentioned this as a point of interest, since the subject had been brought up, and did not think it affected the authors' argument materially.

Mr. Pease replied that the success of a cement job was judged by subsequent

results. Pressure tests applied were purely a matter of field experience, and were based on results. Test pressures were recorded, and if subsequently failures occurred, the company adopted higher test pressures.

MR. TAITT said that the question of the hardening time, whether 1 or 3 days, was one which had only been obtained over a long period of time. He wondered whether any members could give information, based on the results going back as far as they could, as to what time, with cements normally used in the past, had been found suitable. Were there any findings as to what was a suitable time?

50 kg./cm.^{2} strength was based on experience in various parts of the world, but it was quite well known in the Shell group that there was no accurate information as to a fixed suitable time. The group had been making trials in various administrations with reducing the standing times, and as far as it had been out, it had been successful up to the present.

Could members give information as to where failures had occurred through cutting down times too much?

MR. BUSHE, in reply to Mr. Taitt, said that he had found the same thing—namely, that whereas in the past it had been usual to let cement stand for 3 or 4 days, in recent months standing times had been reduced to only 1 day and, as far as he knew, without any ill effects. It might be a point on which they could get together, and there was no reason why the Institute should not approach the Government, if they all accepted the fact that 1 day was sufficiently long.

MR. SCOTT said that in a cementation the actual weakest point was the bond of the cement with the wall, and usually that was very much weaker than the wall of cement, even after 12 hours.

MR. HEALEY replied that he believed one company in the United States had published something about this. They had been doing ordinary cementations with about 50 per cent. failures. Then they had started using wall scratchers on their casing, and had about one failure in fifty.

He believed also in the United States they were now cutting down standing time in certain cases to about 12 hours, and instead of normal cement slurry they were adding gypsum at the end, so that the gypsum was left around the shoe of the casing.

MR. F. H. L. TINDALL (T.L.L.) said that he agreed with Mr. Scott's statement that the bond of the cement with the wall was much more important than the strength of the cement itself. They had been testing their cementation to higher pressures than appeared to be the average in Trinidad, and had found, particularly with surface strings, that they had a large number of failures. The figure quoted by the authors—50 kg./cm.^{2}, *i.e.*, about 750 lb./sq. inch—referred to the strength of the cement, but they had found that the formation appeared weaker than the cement. They had cementation failures at pressures lower than 750 lb. and at depths down to 3000 feet. On occasion they had tried re-cementing, but without any better success. In only a very few cases had there been any signs of circulation returning to the surface, and if the cement itself had been unsatisfactory, then the circulation should have taken the weakest path and returned to the surface. The fact was that there was some portion of the formation which could not stand the test pressures being applied.

In reply to a question concerning Guayaguayare, Mr. Tindall said that he did not consider that conditions on that field were the same as elsewhere. The formation contained large thicknesses of sandy formation which might have some effect on cementation.

In reply to a question, he said that they were now drilling out cementations after 24 hours' setting time, and had not had any evidence of the cement itself proving defective. He attributed the breakdown of the cementation, when test pressures were applied, entirely to the formation and not to the cement.

DR. J. E. SMITH (U.B.O.T.) enquired as to the use of ice in tending to lower the

temperature of cement for deep cementing jobs. He thought it had been used successfully—was it of any real advantage?

MR. HEALEY replied that the difficulty in deep cementations was that the time of placing was so long. If cement were moved after its initial set, it was very much weakened. Ice was used therefore to increase the period of initial set.

MR. SCOTT added that it did also decrease viscosity tremendously.

The discussion then terminated.

MIXED-SOLVENT EXTRACTION.*

By A. V. Brancker, Ph.D., T. G. Hunter, D.Sc., F.Inst.Pet., and A. W. Nash, M.Sc., F.Inst.Pet.

The Function of the Auxiliary Solvent.

Within recent years considerable development has taken place in the use of two or more solvents for solvent-extraction operations. The majority of such developments employ two solvents, and since this also represents the simplest case of multi-solvent refining, two solvent processes only will be dealt with here.

Processes employing two solvents have been divided into two main classes: mixed-solvent processes and double-solvent processes. In mixed-solvent processes both solvents are mutually soluble under the operating conditions—that is, the solvent employed is a homogeneous mixture of the components. In double-solvent processes the two solvents are immiscible or only partly miscible under the operating conditions. The operating temperature, type of stock treated, and relative proportions of the two solvents all affect to a certain degree the class into which any two solvents may be placed. Phenol and water, for example, depending on the temperature and relative amounts of the two components, may be classified as either a mixed or double solvent. These two classes may be further subdivided as follows:—

Mixed Solvents: Type 1.—A solvent mixture of two components in which one solvent is only partly miscible with the stock under the operating conditions, and in which the second solvent is completely miscible with both the first solvent and the stock under the operating conditions.

Type 2.—A solvent mixture of two components in which one solvent is only partly miscible with the stock under the operating conditions, and in which the second solvent is completely miscible with the first solvent, but only partly miscible with the stock.

The type into which a two-component mixed solvent falls will depend to a certain extent on the operating temperature and on the stock treated. A good example of Type 1 mixtures is the benzole–SO_2 process as normally operated. Type 2 mixtures are not so commonly employed as those of the first type; an example is phenol mixed with small quantities of water.

Double Solvents: Type 1.—The extraction with a solvent only partly miscible with the stock under the operating conditions where a second solvent, only partly miscible with the first solvent and completely miscible with the stock under the operating conditions, is employed.

Type 2.—The extraction with a solvent only partly miscible with the stock under the operating conditions where a second solvent, only partly miscible with the first solvent and also only partly miscible with the stock under the operating conditions, is employed.

As before, the type into which the double solvents may be classified will depend to a certain extent on operating temperature and on the stock treated.

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* Paper received 24th March, 1941.

This paper is concerned only with solvent-refining processes employing mixed solvents of Type 1. The first or primary solvent is only partly miscible with the oil at the operating temperature, whilst the second or auxiliary solvent is completely miscible with both the oil and the primary solvent at the operating temperature.

An auxiliary solvent of this nature may be employed for many reasons. The addition of an auxiliary solvent to a primary solvent which is solid at ordinary temperatures,[1] enables extraction to be carried out at lower and more economical temperatures, or at temperatures not practical with the primary solvent alone. In the refining of some heavy oils, particularly those of high viscosity, with a selective solvent, a considerable length of time may be required to obtain separation of the two phases. In these cases the use of an auxiliary solvent to reduce the time of separation and facilitate the sharpness of separation may be employed. The auxiliary solvent in this case is sometimes referred to as an "inert solvent" or "diluent." It has also been claimed that an auxiliary solvent, of the type considered here, in some cases actually improves the refining action of the primary solvent—for example, benzole has been claimed[2] to improve the refining effect of liquid SO_2.

Auxiliary solvents completely miscible with both primary solvent and oil at the operating temperature will be in the main low-boiling hydrocarbons such as propane, petroleum ether, benzole, toluole, and xylole. Auxiliary hydrocarbon solvents of a paraffinic nature, such as propane, may not be completely miscible with some primary solvents under certain operating conditions, and it must be emphasized that the discussion in this paper will not apply under such conditions.

The work described here was undertaken in order to study the effect on extraction brought about by the addition of a completely miscible auxiliary solvent to a primary solvent. The investigation was carried out in two sections. First, the action of an auxiliary solvent was studied for the separation by solvent extraction of a stock consisting of a mixture of two pure substances. In this case the extraction at constant temperature of this stock with a single solvent was ascertained, and then at the same temperature the extraction of the stock with the double-solvent mixture was investigated. Second, the action of an auxiliary solvent was studied on the solvent refining of a mineral oil. As before, extraction at constant temperature with a single solvent followed by extractions with a mixed solvent were compared.

The separation of a binary mixture by solvent extraction and the refining of an oil with a solvent at constant temperature have been shown[3] to be most conveniently studied by means of phase-equilibrium relationships plotted on triangular diagrams. The use of such diagrams enables all the desired variables to be explored quickly and accurately, and this method has been employed here. It has been shown elsewhere[4] that phase-equilibrium relationships at constant temperature for the solvent extraction of a binary stock with a binary solvent mixture—that is, a four-component system—may be adequately represented by means of a regular tetrahedron. It has also been shown[5] that the regular tetrahedron may be used for representing phase equilibrium in an oil mixed-solvent system. Although batch, multiple-contact, and counter-current extraction results can

apparently be computed in an oil-solvent system by means of phase-equilibrium data represented on triangular diagrams,[3] it is not yet known that the tetrahedron diagrams for oil mixed-solvent systems can be used for either multiple-contact or counter-current computations. It is certain, however, that the tetrahedron diagrams can be employed for batch-extraction computations in oil mixed-solvent systems and for batch, multiple-contact, and counter-current extraction computations in four-component systems. The method of carrying out batch-extraction computations by means of such tetrahedron diagrams has been described in detail in another publication,[6] and the use of such diagrams enables the desired variables to be explored, and they have been employed here. All comparisons between single- and mixed-solvent systems have been made on the basis of batch extractions.

Pure-Component Systems.

The pure-component ternary system employed consisted of chloroform, acetone, and water, at a temperature of 25° C. At this temperature chloroform and acetone are completely miscible and represent the binary mixture to be separated by extraction. Water, the principal solvent, is partly miscible with chloroform and completely miscible with acetone at the selected operating temperature of 25° C. Acetic acid, the auxiliary solvent, is completely miscible with water, acetone, and chloroform. Mixtures of chloroform and acetone may be separated by extraction, with a solvent mixture of water and acetic acid at 25° C.

These systems were chosen, not for their industrial importance, but for ease in analysis in terms of individual components, and hence the convenient collection of accurate equilibrium data.

Equilibrium in the three-component system chloroform, acetone, and water at 25° C., and in the four-component system chloroform, acetone, water, and acetic acid at 25° C. was studied, and the detailed investigation of these systems has been described elsewhere.[4-5]

Employing these equilibrium data as a basis for calculation the effect of refining a constant stock with single and mixed solvent was determined. The constant stock selected consisted of 38·5 per cent. acetone, 61·5 per cent. chloroform. In this stock the acetone, by virtue of its miscibility relationships, must be the extracted component, and must be the undesirable component the removal of which is required. In consequence any decrease in acetone content of the raffinate obtained must indicate an improvement in quality.

The following data were computed :—

(1) The effect of solvent/stock ratio on the quality of the raffinate when using the principal solvent alone and mixed with varying amounts of the auxiliary solvent.

(2) The effect of solvent/stock ratio on the yield of raffinate when using the principal solvent alone and mixed with varying amounts of the auxiliary solvent.

The results obtained are given in Table I and shown graphically in Figs. 1 and 2. In Fig. 1, raffinate quality, as denoted by the acetone content of the raffinate, is plotted against solvent stock ratio for different percentages

of auxiliary solvent in the solvent mixtures employed. In this and the remaining figures the principal solvent is referred to as S_1 and the auxiliary solvent as S_2.

TABLE I.

Solvent.	Solvent : Stock ratio.	Weight per cent. yield of raffinate.	Weight per cent. acetone in raffinate.
Water	0·33	94	35·0
,, ...	0·59	90	32·5
,, ...	1·00	85	29·5
,, ...	2·09	76	23·0
,, ...	2·62	73	20·5
Water 80%, acetic acid 20% . .	0·26	93	34·5
,, ,, ,, . .	0·77	90	33·0
,, ,, ,, . .	1·60	80	27·0
,, ,, ,, . .	3·78	67	21·0
,, ,, ,, . .	8·06	56	13·5
Water 61%, acetic acid 39% . .	0·33	94	36·0
,, ,, ,, . .	1·00	85	33·0
,, ,, ,, . .	2·09	69	27·0
,, ,, ,, . .	4·92	44	21·0
,, ,, ,, . .	10·50	32	15·0
Water 55%, acetic acid 45% . .	0·37	94	36·0
,, ,, ,, . .	1·11	81	33·0
,, ,, ,, . .	2·31	56	27·0
,, ,, ,, . .	5·45	17	21·0
Water 48·5%, acetic acid 51·5% .	0·42	92	36·0
,, ,, ,, .	1·26	69	31·5
,, ,, ,, .	2·62	36	27·0
,, ,, ,, .	3·09	23	25·5
,, ,, ,, .	4·00	7	24·5
Water 47·6%, acetic acid 52·4% .	1·29	55	33·0
,, ,, ,, .	2·10	22	31·5

From Fig. 1 it is immediately apparent that better-quality raffinates are obtained at equal solvent/stock ratios for the single solvent than are obtained for any binary solvent mixture. That is, at constant-solvent stock ratio the quality of the raffinate is decreased with any increase in the amount of auxiliary solvent in the solvent mixture employed.

In Fig. 2, raffinate yield, expressed as a weight percentage of the total stock treated, is plotted against solvent-stock ratio for different amounts of auxiliary solvent in the solvent mixtures employed. From this figure it is evident that the yield of raffinate at any constant solvent/stock ratio is highest when extraction with the single solvent is employed. The addition of auxiliary solvent decreases the yield of raffinate obtained.

The extraction obtained using the single solvent may be compared with that obtained using the mixed solvent on the basis of both raffinate yield and quality at constant solvent/stock ratio by considering both Figs. 1 and 2 together. From such a comparison it will be seen that a higher yield of better-quality raffinate is obtained by extraction with the single solvent than by extraction with an equal quantity of mixed solvent. This is illustrated in Fig. 3, in which both yield and quality of raffinate are plotted

against percentage auxiliary solvent in the solvent mixture employed at varying solvent/stock ratios.

The action of the single solvent, whereby a comparatively high yield of good-quality raffinate may be obtained, is definitely impaired by the addition of the auxiliary solvent.

These comparisons have been carried out at equal solvent/stock ratios—that is, equal volumes of single or mixed solvent per volume of stock treated have been employed. Comparisons between the action of single and mixed solvents are sometimes made on a different basis—namely, at equal primary solvent/stock ratios. For example, the results from the

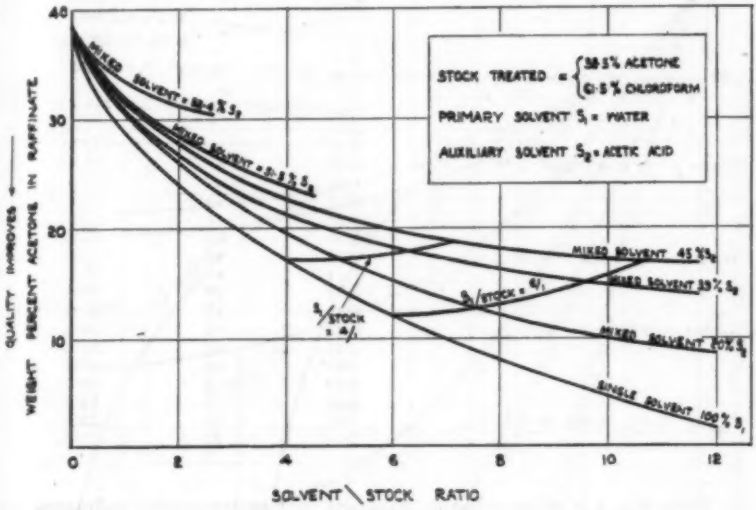

FIG. 1.

extraction of a stock with the principal solvent alone at a solvent/stock ratio of say 3/1 may be compared with the results from the extraction of the same stock with a solvent mixture of primary and auxiliary solvent at a total solvent/stock ratio of say 4/1, and with 25 per cent. of auxiliary solvent in the double solvent employed, but with the principal solvent/stock ratio still constant at 3/1. This method of comparison is very common in patent claims.

In Fig. 1 two curves are included showing comparisons between single-solvent and binary-solvent mixtures on this basis. In these two curves the primary solvent/stock ratio—that is the S_1/stock ratio—has been kept constant at 4/1 and 6/1. The total solvent/stock ratio employed under these conditions is given by the abscissa, whilst the raffinate quality, measured by the weight per cent. acetone in the raffinate, is obtained from the ordinate. These two curves cross the series of curves representing different solvent mixtures starting from the primary solvent curve labelled 100 per cent. S_1, and finally crossing the curve for the solvent mixture

containing 45 per cent. auxiliary solvent, labelled 45 per cent. S_2. Consider, for example, the curve representing a constant principal solvent/stock ratio of 4/1, labelled S_1/stock = 4/1. The raffinate quality when the principal solvent is employed alone at this ratio may be readily ascertained from the 100 per cent. S_1 curve to be 18·0 per cent. acetone. The raffinate quality, when a mixed solvent containing 20 per cent. of auxiliary solvent is employed but in sufficient quantity to keep the principal solvent/stock ratio constant at 4/1, may be obtained from the intersection of the curve labelled S_1/stock = 4/1 with the curve labelled mixed solvent 20 per cent.

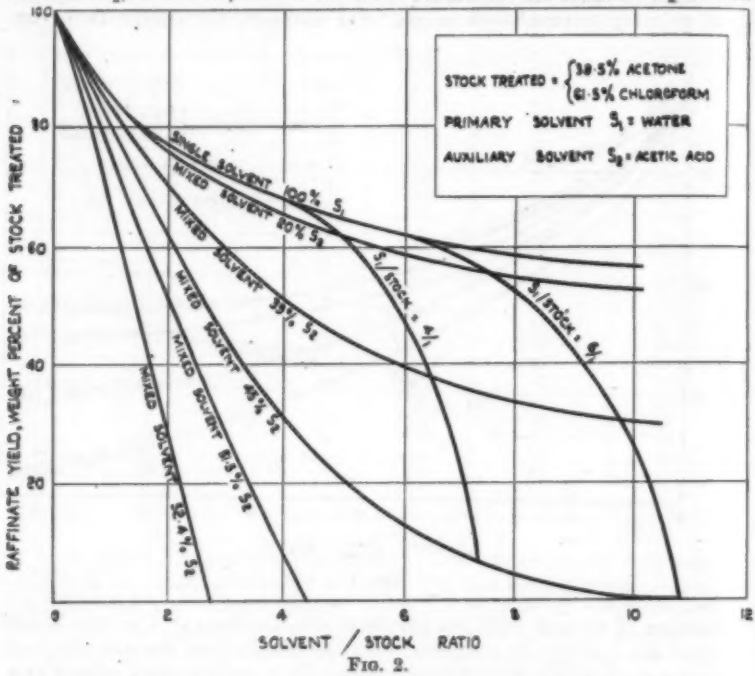

FIG. 2.

S_2. Actually, as will be seen from the figure, this condition is satisfied at a total solvent/stock ratio of 5/1, and the raffinate quality is represented by 18·5 per cent. acetone.

It is obvious from the two curves included in Fig. 1 that raffinate quality becomes poorer when auxiliary solvent is added to the principal solvent on this basis of comparison as well as on the basis of equal solvent/stock ratios.

Two similar curves have been incorporated in Fig. 2, from which it may also be concluded that by this method of comparison the addition of auxiliary solvent decreases the yield of raffinate.

These conclusions have been arrived at from a consideration of a system of four pure components, and it is desirable to decide whether they apply

to the mixed-solvent refining of a complex material like a mineral-oil or a petroleum fraction. Oil single-solvent and oil mixed-solvent systems of similar type were therefore examined.

Oil Solvent Systems.

The single-solvent oil system studied was composed of Anglo-Iranian second cooled blue oil, V.G.C. 0·8553, with acetic acid as the solvent at 25° C. The equilibrium data were represented, in a manner previously described,[3] by means of an equilateral triangle, whereby a physical property is used to characterize the oil. The physical property employed in this case was V.G.C.

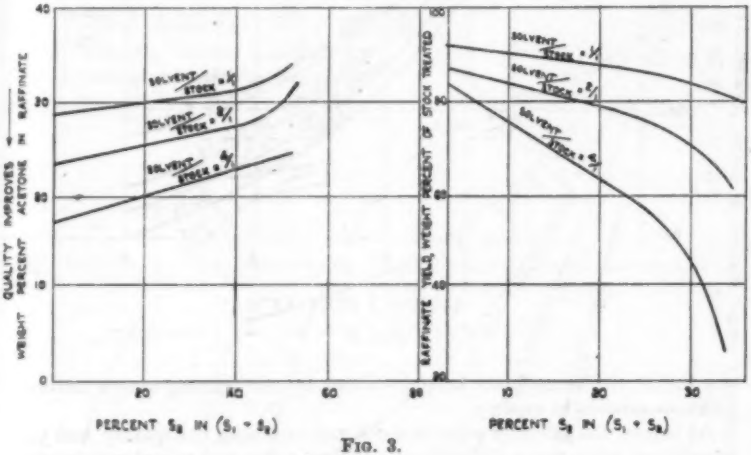
QUALITY IMPROVES → RAFFINATE
WEIGHT PERCENT ACETONE IN
SOLVENT/STOCK = 1/1
SOLVENT/STOCK = 2/1
SOLVENT/STOCK = 4/1
RAFFINATE YIELD, WEIGHT PERCENT OF STOCK TREATED
PERCENT S_2 IN (S_1 + S_2)
PERCENT S_2 IN (S_1 + S_2)

FIG. 3.

The double-solvent oil system investigated consisted of Anglo-Iranian second cooled blue oil, acetic acid and chloroform at 25° C. Acetic acid was only partly miscible with the oil at the selected operating temperature, and is the principal solvent, whilst chloroform, the auxiliary solvent, was completely miscible with both oil and acetic acid. The equilibrium data were represented by means of a regular tetrahedron with the oil characterized by V.G.C. This and the single-solvent system have been reported in detail in another publication.[5]

These two systems are not of any special industrial significance, but were selected for ease in the determination of equilibrium data. No significance is to be attached to the use of acetic acid and chloroform in the two cases investigated. Accurate methods of analysis of oil-acetic-acid and of oil-acetic-acid-chloroform mixtures were available, whilst raffinate and extract phases formed by the addition of these solvents to the oil separated readily without entrainment or hold up of droplets of one phase within the other. The equilibrium data obtained are believed to be accurate and reliable.

These data were used as a basis for calculating the effect of refining the second cooled blue oil with single and mixed solvents. Any decrease in

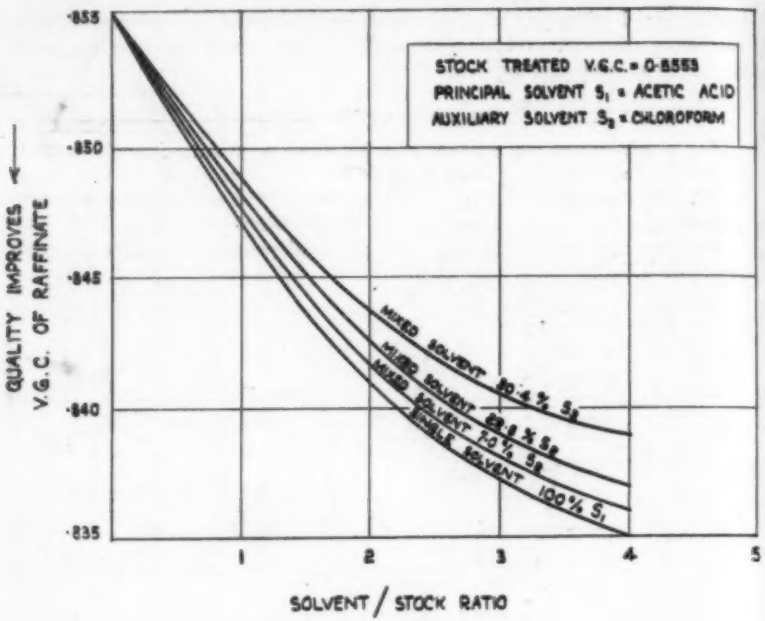

FIG. 4.

the V.G.C. of the raffinate brought about by the refining action indicates an improvement in quality.

As before, the effect of solvent/stock ratio on both the quality and yield of raffinate when using the principal solvent alone and mixed with varying

TABLE II.

Solvent.	Solvent : Stock stock.	Weight per cent. yield of raffinate.	V.G.C. of raffinate.
Acetic acid	1·0	92	0·8473
" "	2·0	87	0·8408
" "	3·0	85	0·8374
" "	4·0	84	0·8351
Acetic acid 93%, chloroform 7%	1·0	90	0·8479
" " "	2·0	84	0·8415
" " "	3·0	79	0·8382
" " "	4·0	75	0·8360
Acetic acid 77·2%, chloroform 22·8%	1·0	86	0·8482
" " "	2·0	75	0·8426
" " "	3·0	66	0·8393
" " "	4·0	56	0·8370
Acetic acid 69·6%, chloroform 30·4%	1·0	81	0·8485
" " "	2·0	63	0·8436
" " "	3·0	45	0·8406
" " "	4·0	27	0·8390

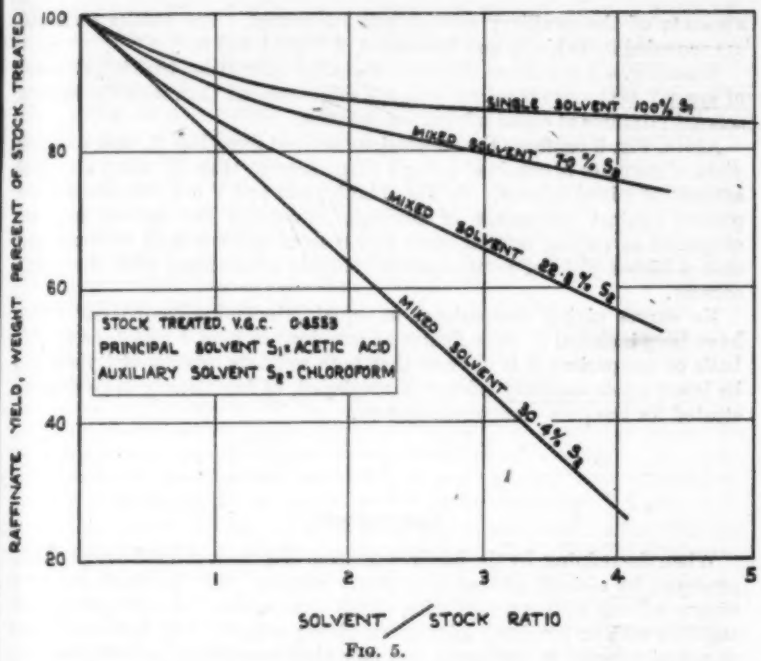
RAFFINATE YIELD, WEIGHT PERCENT OF STOCK TREATED
100
80
60
40
20
SINGLE SOLVENT 100% S1
MIXED SOLVENT 7.2 % S2
MIXED SOLVENT 22.8 % S2
MIXED SOLVENT 30.4% S2
STOCK TREATED, V.G.C. 0·8553
PRINCIPAL SOLVENT S1 = ACETIC ACID
AUXILIARY SOLVENT S2 = CHLOROFORM
1
2
3
4
5
SOLVENT / STOCK RATIO

FIG. 5.

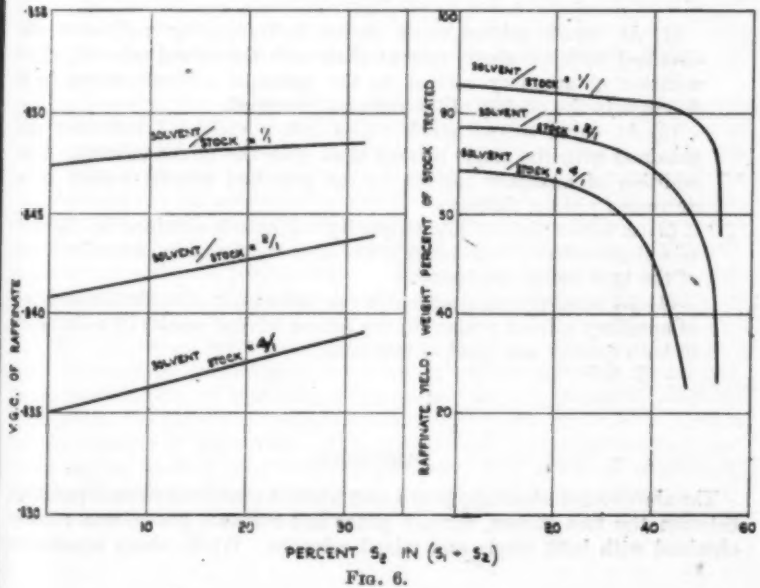
V.G.C. OF RAFFINATE
·850
·845
·840
·835
·830
SOLVENT/STOCK = 1/1
SOLVENT/STOCK = 2/1
SOLVENT/STOCK = 4/1
10
20
30
RAFFINATE YIELD, WEIGHT PERCENT OF STOCK TREATED
100
90
80
70
60
40
20
SOLVENT/STOCK = 1/1
SOLVENT/STOCK = 2/1
SOLVENT/STOCK = 4/1
20
40
60
PERCENT S2 IN (S1 + S2)

FIG. 6.

amounts of the auxiliary solvent was computed. The results obtained are recorded in Table II and illustrated in Figs. 4 and 5.

From Fig. 4 it is evident that better-quality raffinates—that is, raffinates of lower V.G.C.—are obtained with the single-solvent than with the binary-solvent mixtures at equal solvent/stock ratios.

Again, Fig. 5 confirms the conclusions derived from Fig. 2, that a higher yield of raffinate is obtained using a single solvent than by using an equal amount of mixed solvent. In Fig. 6 both yield and V.G.C. of raffinate are plotted against percentage of auxiliary solvent in the solvent mixture employed at varying solvent/stock ratios, from which it may be concluded that a higher yield of better-quality raffinate is obtained with the single solvent.

No curves giving comparisons at equal principal solvent/stock ratios have been included in these figures as was done in Figs. 1 and 2, as on this basis of comparison it is obvious that both raffinate quality and yield will be lower when auxiliary solvent is employed, as has already been demonstrated for the pure-component system.

Conclusions.

When the refining, by the batch extraction of a stock of fixed composition, produced by a single solvent only partly miscible with the stock and by a binary solvent mixture, consisting of the same solvent as principal solvent together with an auxiliary solvent completely miscible with both stock and principal solvent, is compared, the following conclusions are obtained :—

(1) At equal solvent/stock ratios better-quality raffinates are obtained with the single solvent than with the mixed solvent. The addition of auxiliary solvent to the principal solvent results in a decrease in the quality of the raffinate produced.

(2) At equal solvent/stock ratios better yields of raffinates are obtained with the single solvent than with the mixed solvent. The addition of auxiliary solvent to the principal solvent results in a decreased yield of raffinate.

(3) A better yield of higher-quality raffinate is obtained by the use of a single solvent than would be obtained by the use of mixed solvent of the type being considered.

(4) At equal principal solvent/stock ratios an increase in the amount of auxiliary solvent present in the mixed solvent results in a decrease in both quality and yield of raffinate.

Discussion.

The above conclusions apply to a case where a sharp and clean separation between the two phases, extract phase and raffinate phase, was readily obtained with both single and mixed solvents. Where sharp separation

between phases cannot be easily obtained with the single solvent, but can be so obtained by the addition of auxiliary solvent, then it is possible for mixed-solvent extraction to show improved results compared with single-solvent extraction. Complete phase separation may be very slow, owing to inadequate gravity differential between phases, or to the high viscosity of one or both phases, at the operating temperature. Sometimes, if the oil being treated is very dark, the demarcation line between phases is difficult to observe clearly, and poor separation may result through errors in judgement by the operator. From the continued investigation of liquid-liquid equilibria and solvent-extraction processes over a period of years, it is the considered opinion of the authors that clean phase separation is a matter of some difficulty. Hence, either one or both phases, but more often both, may contain entrained droplets. A raffinate, obtained by the removal of solvent from a raffinate phase containing entrained extract phase, would be of inferior quality to the raffinate obtained from the same raffinate phase free from entrained extract phase. Further, it is possible for the results of solvent refining with a single solvent where phase entrainment has occurred to be less favourable than the results obtained with a mixed solvent where entrainment is absent. In many mixed solvents the auxiliary solvent is of low viscosity such as benzene, and its addition speeds up and improves phase separation. Under such conditions mixed-solvent refining may prove practically advantageous when compared with single-solvent refining. The reported improvement [7, 8] brought about by extraction with benzole–SO_2 compared to extraction with liquid SO_2 alone in the treatment of lubricants and heavy oils is probably due to this effect. In any entrainment free extraction process liquid SO_2 should always give better results than SO_2–benzole. In actual practice, by reducing entrainment the addition of benzole can improve the extraction of liquid SO_2. This fact has not always been recognized, and erroneous explanations as to the function of the benzole [2, 8] have been advanced.

In comparing the action of mixed solvents, care is not always taken to ensure that the mixed solvents compared are of similar type. The type or class investigated here is one in which the auxiliary solvent is miscible with both stock and principal solvent. For example, the mixed solvent aniline–benzene at ordinary temperatures comes within this category, whereas the double solvent aniline–petroleum ether at ordinary temperatures does not, since aniline and petroleum ether are usually only partly miscible at ordinary temperatures. Nevertheless such cases have been compared without recognition of the fact that their action may be different.

While the use of an auxiliary solvent of the type considered here in a mixed-solvent-extraction process may have certain practical advantages, such as reduction of operating temperature and improvement of phase separation, the general effect is to increase the solvent power of the solvent at the expense of selectivity. This gives rise to a decrease in yield and decrease in quality of resulting raffinates. Any practical advantages obtained by the addition of auxiliary solvent must be considered in conjunction with these disadvantages.

References.

[1] U.S.P. 2,084,471 (1937).
[2] U.S.P. 1,945,516 (1934).
[3] Hunter, T. G., "The Science of Petroleum," Vol. 3, 1818 (1938).
[4] Brancker, Hunter, and Nash, *J. Physical Chem.*, 1940, **44**, 683.
[5] Brancker, Hunter, and Nash, *Industr. Engng. Chem.*, 1941, **33**, 880.
[6] Hunter, T. G., *ibid.*, to be published.
[7] Thompson, "The Science of Petroleum," Vol. 3, 1856 (1938).
[8] Dofize, J. C. L., "On the Edeleanu Process," pp. 142–206 (1937).

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